

Calculation of Molecular Vibrations: Selective Scaling Factors for Semiempirical Force Constants

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Received 12 May 1997; accepted 31 July 1997

ABSTRACT: The complete force constant matrices of a set of 50 aliphatic and aromatic hydrocarbons are calculated at the density functional theory B3LYP/6-31 + G(*d*, *p*) and semiempirical PM3 levels of theory. After transformation from Cartesian to nonredundant internal coordinates, the errors in the semiempirical force constants are systematically analyzed. The force constants of the C—C stretching coordinates can be easily corrected by a second-order fit. Thus, only two parameters are needed to reduce the mean error from 21.2 to 1.23%. The errors of other internal coordinates, particularly those including torsional modes, exhibit a larger diversity. The performance of the correction scheme in predicting vibrational spectra is shown for several examples including buckminsterfullerene (C₆₀). © 1997 John Wiley & Sons, Inc. *J Comput Chem* 18: 2050–2059, 1997

Keywords: complete theoretical force fields; force constants; DFT methods; semiempirical methods; vibrational spectra

Introduction

Methods for computing the energies of vibrational transitions and their intensities have become a useful tool for structure determination, mainly of small and reactive molecules.^{1–3} Quadratic force fields from density functional theory (DFT) have been shown to give especially excellent

results for vibrational spectra^{4–9} and more recently for the calculation of vibrational circular dichroism (VCD) intensities.^{9,10} Even though DFT methods are computationally less demanding than *ab initio* calculations of comparable accuracy,¹¹ energy second derivatives are still too expensive for the majority of systems that are interesting for synthetic chemists (> 50 atoms, no symmetry).

Pure empirical force fields^{12,13} are practicable for large molecules and it is possible to fit the analytic form of the empirical potential function to

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reproduce experimental vibrational frequencies.¹⁴ However, only a limited number of cross-terms are included in empirical potential functions, making the description of strongly coupled systems difficult. Our approach to predict vibrational frequencies of large molecules therefore refers to calculations of the complete energy second derivative matrices on the basis of molecular orbital calculations.

Semiempirical Hartree–Fock (HF) methods are now amenable to molecules containing hundreds of atoms. Due to approximations of the semiempirical model, MNDO-based methods, however, exhibit relative large errors in predicting force constants and vibrational energies. Unfortunately the errors are not systematic and there is no overall scaling factor for improving the accuracy.¹⁵

Nevertheless, early studies in the 1970s showed that, in principle, transferable scaling factors for HF force constants, even at the semiempirical level of theory, can be derived by fitting them to experimental vibrational energies.^{11–14} There are two main reasons that restricted the use of scaled semiempirical force fields for large molecules to a limited number of applications.^{15–26}

1. In contrast to *ab initio* HF force constants, which exhibit a quite systematic error, semiempirical force fields have to be corrected with distinct factors for different internal coordinates to obtain a reasonable fit for computed frequencies.
2. Only a limited number of molecules with reliably assigned experimental normal modes are available to scale the theoretical force constants.

General Approach

To avoid the latter problem we derived correction factors by fitting PM3²⁷ force constants to those obtained with the Becke3LYP/6–31 + G(*d*, *p*) method.^{28,29} Contrary to the availability of experimental frequencies, the data set of accurate DFT force constants is in principle not limited and can be easily extended to new elements or functional groups.

For a first study we restricted our approach to pure hydrocarbons and computed semiempirical and DFT force constants of a set of 50 small and medium sized structures (see Fig. 1). As the reference method for our scaling procedure we chose

the DFT method with a 6–31 + G(*d*, *p*) basis as a reasonable compromise between accuracy and computational cost.

For the development of a selective scaling method, transformation of the Hessian matrix from Cartesian to suitable internal coordinates³⁰ is a prerequisite. The set of internal coordinates has to be complete and nonredundant, otherwise the truncated Taylor expansion of the molecular potential energy *V* in eq. (1) is not unique and the transferability of correction factors is not ensured. *S_i* are the internal coordinates and *F_{ij}* are the force constants

$$V = V_0 - \sum_i \phi_i S_i + \frac{1}{2} \sum_{i,j} F_{ij} S_i S_j + \frac{1}{6} \sum_{i,j,k} F_{ijk} S_i S_j S_k + \dots \quad (1)$$

Generally, vibrational frequencies are not very sensitive toward errors in the off-diagonal elements of the Hessian matrix. However, in the case of strongly coupled molecular systems, off-diagonal elements can have a large impact on the calculated vibrational energies. A suitable coordinate system minimizes the off-diagonal terms and allows a scaling scheme, which is based on the correction factors for the diagonal elements of the Hessian. We used a program developed by Pulay et al.,³¹ which generates the natural internal coordinates automatically (at least for a wide range of structural patterns).

Computational Methods

All energy second derivative calculations were done at the fully optimized geometries. The force constants were evaluated by analytical second differentiation at the DFT level and by numerical differentiation of the analytical first derivatives at the semiempirical level. The calculations were performed using the G94-C.3 release of the Gaussian programs.³² The Cartesian force constant matrices and dipole moment derivatives were transformed²⁸ into internal coordinates. The resulting data base with more than 1000 pairs of semiempirical and Becke3LYP diagonal force constants was used to derive multiple scaling factors for the PM3 force constants according to eq. (2),

$$F'_{ii} = cF_{ii}, \quad (2)$$

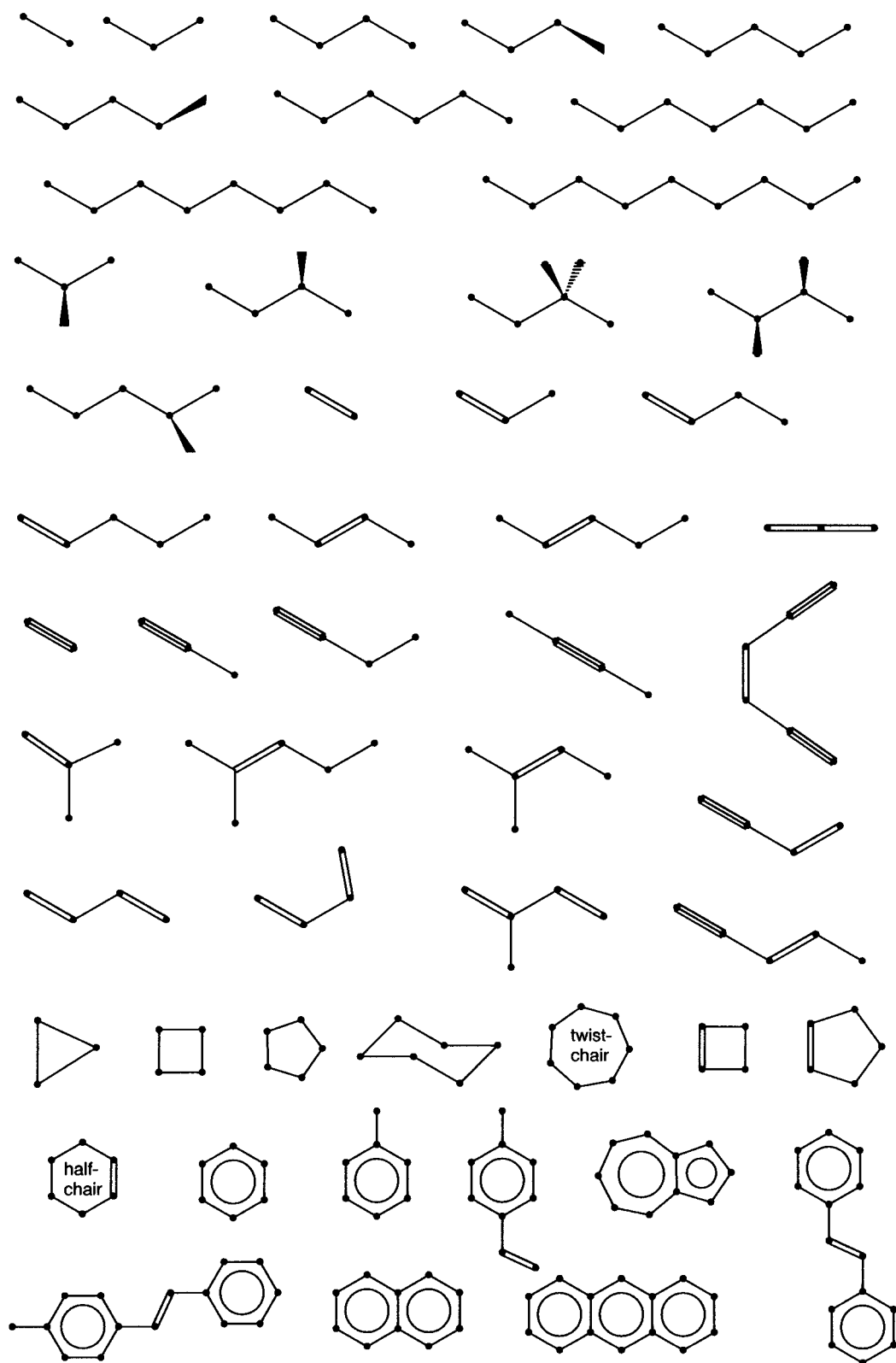


FIGURE 1. Set of hydrocarbon structures that were used to compare semiempirical and DFT force constants.

where F'_{ii} is the scaled diagonal force constant, F_{ii} is the original one, and c is the scaling factor. The off-diagonal force constants were not determined independently but were calculated as the geometric mean of the corresponding diagonal scale factors,

$$F'_{ij} = (c_i c_j)^{0.5} F_{ij}. \quad (3)$$

The number of factors was kept as small as possible by grouping appropriate coordinates with similar scaling factors. The different groups of internal coordinates are described in the following paragraphs.

Results

STRETCHING FORCE CONSTANTS

It is well known that theoretical C—C stretching force constants are strongly overestimated if electron correlation is not adequately considered. This holds especially for the semiempirical HF level of theory as seen in Figure 2, where the uncorrected PM3 C—C stretching force constants of our hydrocarbon data set are plotted as a function of the Becke3LYP/6-31 + G(d, p) values.

The mean deviation of all uncorrected semiempirical C—C stretching force constants from the DFT results is 21.2% (1.875 aJ/Å²). We found different errors (see Fig. 3), depending on the C—C bond order: 26% in the single C—C bond of ethane, 21% in the C=C bond of ethylene, and 5% in the C≡C triple bond of acetylene. This illustrates the difficulties for an overall scaling¹² of PM3 force constants and emphasizes the need for a selective correction scheme.

However, surprisingly good results are obtained if different scaling factors are used for different types of bonds (see Table I). The correlation graph in Figure 4 compares the corrected PM3 stretching force constants with Becke3LYP/6-31 + G(d, p) values. The correlation coefficient is 0.9986 (0.9871 without correction). After correction the mean deviation of all C—C stretching force constants went from 21.2 to 1.23% (0.17 aJ/Å²). A comparable result (correlation coefficient 0.9959) was obtained with a parabolic fit. In eq. (4) F'_{C-C} are the scaled stretching force constants and F_{C-C} are the unscaled values, respectively.

$$F'_{C-C} = a \cdot F_{C-C}^2 + b \cdot F_{C-C} + c, \quad (4)$$

where $a = 0.031$, $b = 0.263$, and $c = 0.711$.

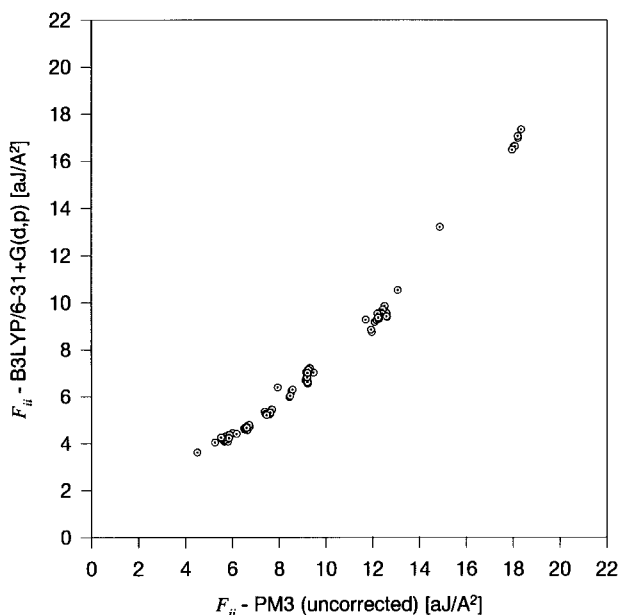


FIGURE 2. Uncorrected PM3 C—C stretching force constants compared with B3LYP/6-31 + G(d, p) data. The mean deviation of the semiempirical stretching force constants is 21.2%.

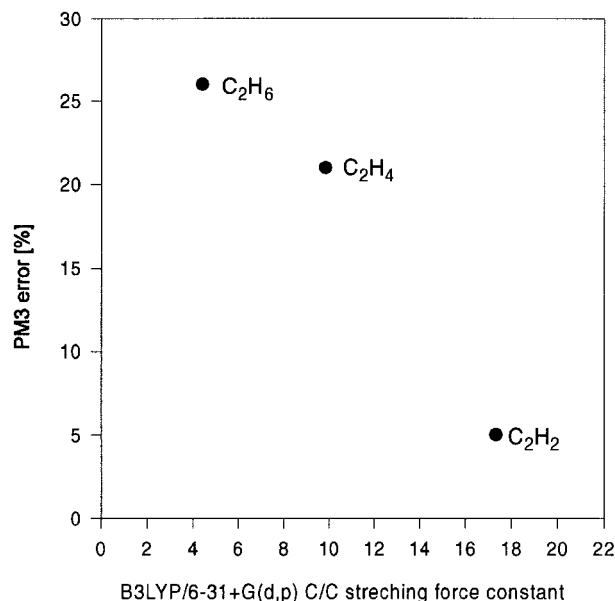


FIGURE 3. The error in PM3 C—C stretching force constants as a function of their magnitude calculated with B3LYP/6-31 + G(d, p). The three data points correspond to the diagonal elements of the Hessian matrix for the C—C stretching coordinate in acetylene, ethylene, and ethane, respectively.

TABLE I.
Scaling Factors for PM3 Force Constants.

Deformational Coordinate	Mean Deviation (%)		<i>n</i>	Scaling Factor
	Uncorrected	Corrected		
C _{sp} ³ —C _{sp} ^{2/sp} single bond	42.0	→	37	0.7041
C _{sp} ³ —C _{sp} ³ single bond	32.4	→	97	0.7410
C ÷ C aromatic bond	32.1	→	80	0.7513
C=C double bond	30.4	→	26	0.7663
C≡C triple bond	7.6	→	7	0.9288
C—C _{sp} ³ —C bendings	13.8	→	57	0.882
C—C _{sp} ² —C bendings	5.75	→	67	1.048
C—C _{sp} ¹ —C bendings	19.7	→	18	0.835
CH ₃ bendings	6.03	→	304	1.055
CH ₂ (scissoring)	12.2	→	58	1.139
CH ₂ (rocking)	2.80	→	58	1.016
CH ₂ (wagging)	5.07	→	58	1.053
CH ₂ (twist)	17.9	→	58	1.219
C=CH ₂ (wagging)	21.5	→	16	0.822
C=CH ₂ (rocking)	10.7	→	16	1.134
C=CH ₂ (scissoring)	18.1	→	16	1.223
C—H (oop) aliphatic	15.9	→	17	0.860
C—H (oop) ring	8.02	→	41	1.075
C—H (rocking) aliphatic	17.2	→	17	1.210
C—H (rocking) ring	13.2	→	41	1.125
C=C torsion	27.9	→	56	1.387
C—C torsion	35.8	→	101	1.752

n, Number of force constants used for the least squares fit.

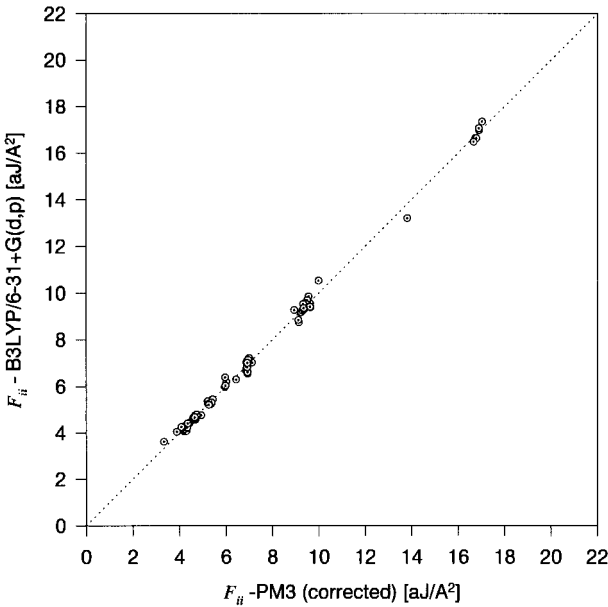


FIGURE 4. Corrected PM3 C—C stretching force constants compared with B3LYP/631 + G(*d*, *p*) values. For correction factors, see Table III. The mean deviation of the corrected semiempiric stretching force constants is 1.23%.

PM3 stretching force constants of carbon—hydrogen bonds seem to reproduce the Becke3LYP/6–31 + G(*d*, *p*) values with a sufficiently high accuracy (scaling factor: 1.0059). Because of the unique anharmonicity of the C—H stretching modes, calculations, which are based on the harmonic approximation, predict these modes at ~ 10% too high on energy compared to experimental results.

DEFORMATIONAL FORCE CONSTANTS

Similar to the stretching force constants, there is no overall scaling factor for deformational coordinates. Grouping of the deformational internal coordinates into sets with common scaling factors is less successful than in the case of stretching coordinates. Some deformations are overestimated (most of the open chain C—C—C bendings), some are underestimated (C—C—H, H—C—H bending force constants), and other groups of semiempirical force constants are close to the DFT results (Table I).

TORSIONAL CONSTANTS

Exact torsional potential functions are of particular interest for conformational studies of large molecules or polymers.³³ The absolute values of torsional force constants are one order of magnitude lower than those for stretching force constants, which gives rise to larger errors. The PM3 calculated C=C double bond torsional constants on average are too low by 27.9% compared to the DFT values. The error seems to be reasonably systematic because it can be reduced by scaling to 7.2%. However, there is no simple scaling procedure for correction of the large error in C—C single bond torsional constants. By scaling with a factor of 1.752, the error only drops from 35.8 to 23.4%.

Examples

Using the scaled force fields the frequencies of the PM3 calculated vibrational modes should be much closer to the DFT values and thus to the experiment than those determined with the standard PM3 method. Scaling should also improve the computed intensities due to a better reproduction of the displacement vectors of the atoms in the normal mode vibrations. The performance of our scaling procedure is exemplified in the following using ethylene, benzene, and C₆₀ as examples.

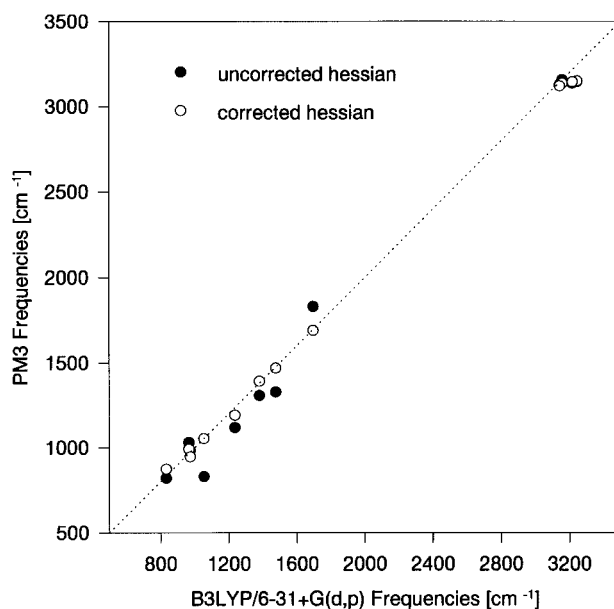


FIGURE 5. Frequencies of the PM3 calculated (●) uncorrected and (○) corrected vibrational normal modes of ethylene compared with those calculated at the B3LYP/6-31 + G(*d*, *p*) level.

ETHYLENE

The PM3-uncorrected, PM3-corrected, and DFT vibrational frequencies calculated therefrom are shown in Table II and Figure 5. The mean devia-

TABLE II.
Calculated Vibrational Frequencies of Ethylene Based on Uncorrected and Corrected PM3, and DFT Force Fields.

Symmetry (Description)	B3LYP / 6-31 + G(<i>d</i> , <i>p</i>)	PM3		SQM ³⁶	Exp. ³⁷
		Uncorrected	Corrected		
In plane					
B _{2u} (CH ₂ asymmetric stretch)	3243	3145	3150	3120	3105
B _{1g} (CH ₂ asymmetric stretch)	3216	3136	3144	3092	3086
A _g (CH ₂ symmetric stretch)	3156	3156	3136	3042	3026
B _{3u} (CH ₂ symmetric stretch)	3141	3127	3120	3022	3021
A _{1g} (C = C stretch and CH ₂ scis)	1695	1829	1685	1626	1630
B _{3u} (CH ₂ scis bend)	1475	1328	1469	1455	1444
A _{1g} (CH ₂ scis bend and C = C stretch)	1380	1307	1391	1345	1342
B _{1g} (CH ₂ rocking bend)	1236	1093	1205	1222	1220
B _{2u} (CH ₂ rocking bend)	833	821	874	821	826
Out of plane					
A _{1u} (C = C torsion)	1054	881	1054	1025	1023
B _{1u} (CH ₂ wagg out of plane)	974	1054	993	940	951
B _{2g} (CH ₂ wagg out of plane)	967	984	946	949	933

tion of the uncorrected PM3 frequencies of 80.2 cm^{-1} (compared to DFT) drops to 27.2 cm^{-1} upon scaling. The improvement is most dramatic for the C=C stretching mode (A_{1g}), which by scaling is shifted to lower wave numbers by 144 cm^{-1} , the CH_2 rocking bend mode (B_{1g}), which is corrected toward higher wave numbers by 112 cm^{-1} , and the C=C torsional mode (A_{1u}), which is moved toward lower wave numbers by 173 cm^{-1} . Moreover, the C=C torsional frequency (A_{1u}) and the CH_2 wagging (B_{1u}), which are interchanged by the standard PM3 method, appear in the correct sequence after scaling. This could not have been achieved with a single scale factor for the force constants or vibrational frequencies.

BENZENE

In Figure 6 PM3-uncorrected and PM3-corrected frequencies of the vibrational normal modes of benzene are plotted as a function of the B3LYP/6-31 + $G(d, p)$ values. Using our scaling procedure the mean deviation of the standard PM3 frequencies of 57.1 cm^{-1} is reduced to 21.9 cm^{-1} . Based on the corrected PM3 force field, the energy of the twofold degenerate E_{2g} C—C stretching mode is computed at 1614 cm^{-1} (B3LYP frequency: 1630 cm^{-1}) compared to 1786 cm^{-1} according to standard PM3. One of the most prominent benzene normal modes, the totally symmetric A_{1g} "breathing" mode, which is calculated 136 cm^{-1} too high at the uncorrected PM3 level, is scaled down to 1060 cm^{-1} (1011 cm^{-1} at B3LYP).

Figure 7 shows the experimental gas phase Raman spectrum³⁸ of benzene, the B3LYP/6-31 + $G(d, p)$ calculated spectrum, and the corrected and uncorrected PM3 results. It is evident that not only the numerical values (see Table III) of the frequencies are corrected but also the "general pattern" of the spectrum fits closer to the experimental and DFT results. Upon scaling, the A_{1g} C—C stretching mode and the E_{2g} ring-H out of plane mode swap places and appear in their correct relative position.

BUCKMINSTERFULLERENE

There are 174 fundamentals in C_{60} , but only four of them are IR active (T_{1u} symmetry).³⁵ Thus, the assignment of theoretical and observed IR normal modes is simplified and unambiguous. In a molecular framework as rigid as C_{60} , torsional

modes can be neglected in a first approximation. Because the scale factor for C— C_{sp^2} —C bendings is close to unity (Table I), errors in the C—C stretching force constants should account for most of the deviations of PM3 calculated vibrational frequencies compared to observed spectra. Therefore, we restricted our scaling procedure to the correction of the C—C stretching force constants and the corresponding diagonal elements. Thus, only a single factor of 0.7513 was used for scaling the C—C force constants in aromatic bonds (Table 1).

The IR active fundamental frequencies based on the corrected and uncorrected PM3 force field are given in Table IV. Calculated and experimental IR spectra (KBr matrix) are shown in Figure 8. Similar to the previous examples, the very large error ($\sim 300\text{ cm}^{-1}$ for the highest T_{1u} vibration) in the semiempirical description of stretching modes is strongly reduced and the corrected pattern of the IR spectrum fits well to the experimental one.

Note that the IR allowed fundamental vibration with the lowest frequency at 557 cm^{-1} (Exp. 528 cm^{-1}) remains almost unchanged after scaling, because it almost exclusively involves deformational modes.

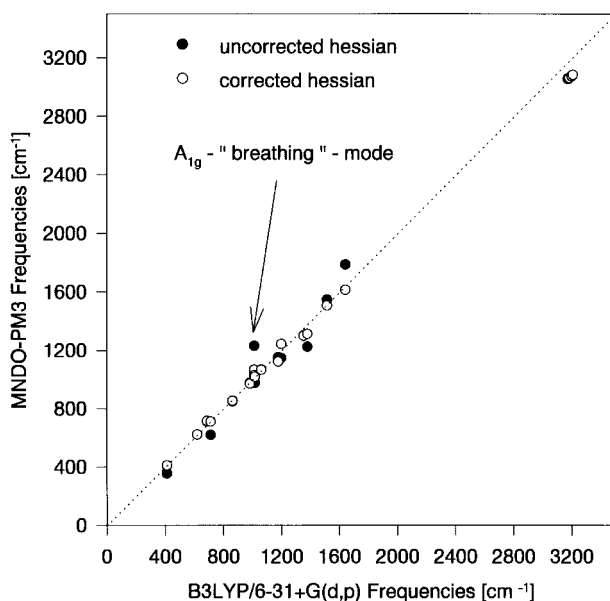


FIGURE 6. Frequencies of the PM3 calculated (●) uncorrected and (○) corrected vibrational normal modes of benzene compared with those calculated at the B3LYP/6-31 + $G(d, p)$ level.

TABLE IV.
Calculated IR Active Vibrational Frequencies of C₆₀
Based on Uncorrected and Corrected PM3 Force
Fields and Experimental (KBr-Matrix) Results.

Symmetry	PM3		Exp. ³²
	Uncorrected	Corrected	
T _{1u}	557	556	528
T _{1u}	733	638	577
T _{1u}	1377	1246	1183
T _{1u}	1708	1481	1429

Conclusions

We calculated the complete force constant matrices and frequencies of vibrational normal modes of a set of 50 hydrocarbons with the semiempirical PM3 method and at the B3LYP/6-31 + G(*d*, *p*) level of DFT. The semiempirical method exhibits very large and moreover unsystematic errors (-200 to $+300$ cm⁻¹) in predicting the fundamen-

tal vibrational frequencies, whereas the DFT method is very close to the experiment.

Based on our results the use of DFT results to scale semiempirical force constants is justified. This procedure is much simpler and less prone to errors than the usual fitting of semiempirical force constants to experimental vibrational frequencies. Because of the unsystematic nature of the errors of the semiempirical method, there is no overall scaling factor to improve its accuracy. The scaling factors range from 0.704 for the stretching of C—C single bonds to 1.752 for torsional force constants around C—C single bonds. However, specific scale factors for similar types of natural internal coordinates that are particular for stretching modes can be derived. Their use greatly improves the accuracy of the force constants compared to DFT.

Consequently the vibrational frequencies calculated from the force constant matrices corrected by our multiple scale factors are much closer to the experiment (IR and Raman) than those calculated by the standard PM3 method. In the case of ethylene and benzene, not only the magnitude but also

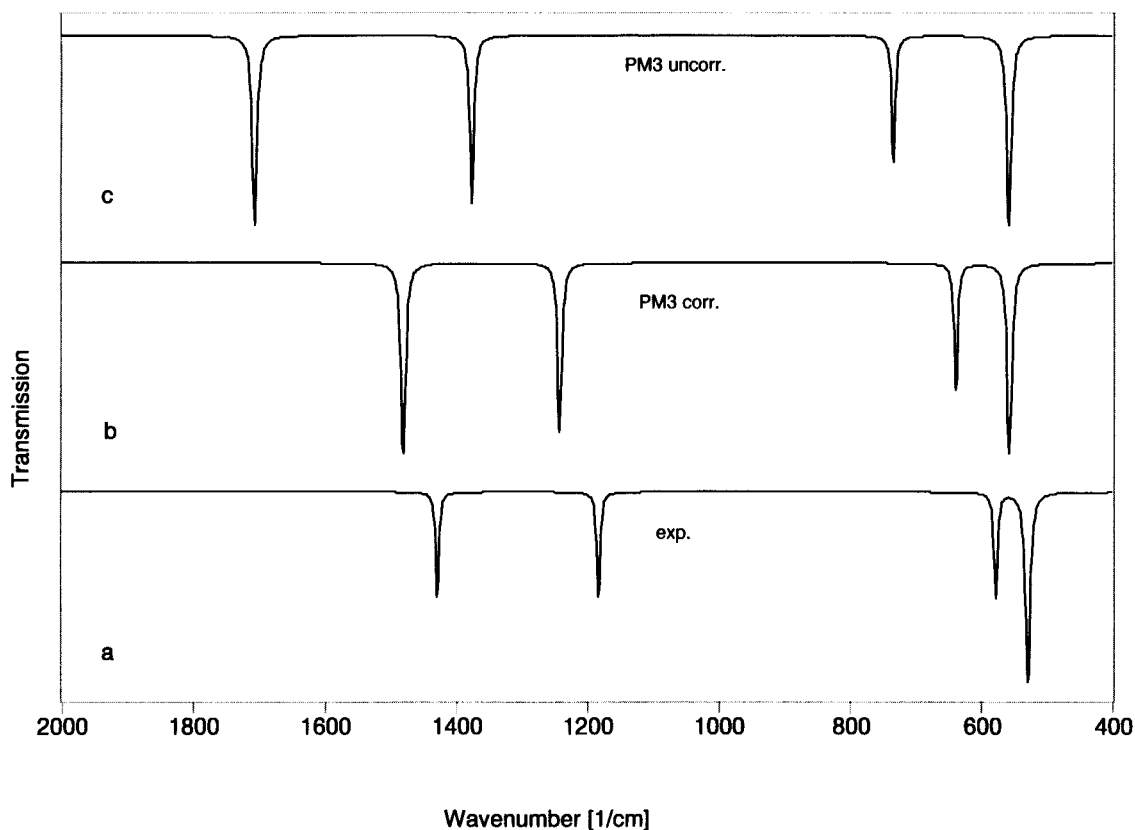


FIGURE 8. IR spectrum of C₆₀. (a) Experimental spectrum⁴⁰ (KBr matrix) redrawn with a standard bandwidth of 5 cm⁻¹. (b) theoretical spectrum at the corrected PM3 level. (c) Theoretical spectrum at the uncorrected PM3 level.

the sequence of vibrational frequencies is corrected.

The scaling procedure can be reduced to a single scale factor in the case of C_{60} and most probably for other fullerenes and rigid cage molecules, because the errors are mainly located in the C—C stretching modes. The force constants of these modes exhibit an error that can be corrected (from 21.2 to 1.23%) by a second-order fit. This can be easily implemented in semiempirical programs.

Even though the scaled semiempirical method is less accurate than high level *ab initio* or DFT methods (to which it was fitted), we think it is of practical use for calculating IR and Raman spectra of hydrocarbons, particularly rigid cage molecules like fullerenes, which are too large to be treated with more advanced methods.^{41–43} In principle, parametrization could be extended to other elements. However, there is a practical limit because the number of scale factors for different internal coordinates increases drastically with the number of elements included in the parametrization.

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